

ON THE RAMAN SPECTRUM OF THIANTHRENE IN THE SOLID STATE

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Plate XIII

ABSTRACT. The Raman spectrum of thianthrene in the solid state has been studied for the first time. The substance is highly fluorescent; but by using special technique the continuous fluorescent background has been considerably suppressed and the substance in the solid state has yielded 11 Raman lines not recorded before. These lines are at 3044(6), 2912(2), 2462(2), 1571(4), 1275(4), 1125(10), 1033(10), 650(4), 561(4), 319(4), 241(4), 159(4), 85(2) and 62(2) cm^{-1} respectively. An anti-stokes line at 159(2) cm^{-1} has also been observed.

The strongest characteristic shifts are at 1125 and 1033 cm^{-1} respectively. The frequency due to the C-S linkage is found at 650 cm^{-1} .

INTRODUCTION

It appears that the Raman spectra of linear tricyclic compounds have not been studied in any detail. This is perhaps due to the fact that these compounds are highly fluorescent under the radiation of the mercury arc, and require a laborious process of purification for obtaining the Raman spectra. The only reference to the Raman spectra of such compounds appears in the works of Ansidei (1936, 37). Anthracene is the simplest compound of this series and its structural formula is as follows :

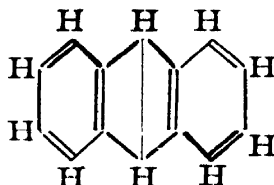


Fig. 1a

If the two CH groups in the para positions in the central ring of anthracene be substituted by S atoms, thianthrene is formed. Its structural formula is as follows :

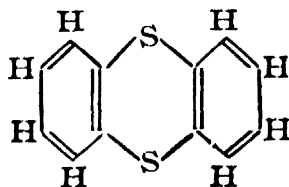


Fig. 1b

The substitution of the two CH groups by S atoms produces a reorientation of the valency bonds inside the benzene ring. It would, therefore, be an interesting study to examine the effect of this substitution. The structures of anthracene and thianthrene then become entirely different from one

another, and we should, therefore, not expect any similarity between the Raman spectra of the two compounds.

EXPERIMENTAL

Thianthrene, obtained from the Research Laboratory of Eastman Kodak Co., was purified by repeated crystallization with extra pure benzene till perfectly transparent crystals were obtained. These crystals scattered sufficient light to produce the Raman spectrum on the plate but the fluorescence on the plate was very intense and no Raman lines could be observed until the crystals were melted in the Raman tube and allowed to solidify slowly. The solidified mass, on exposure to the light of the mercury arc filtered through a concentrated solution of sodium nitrite, yielded 14 new Raman lines, not recorded before.

TABLE I

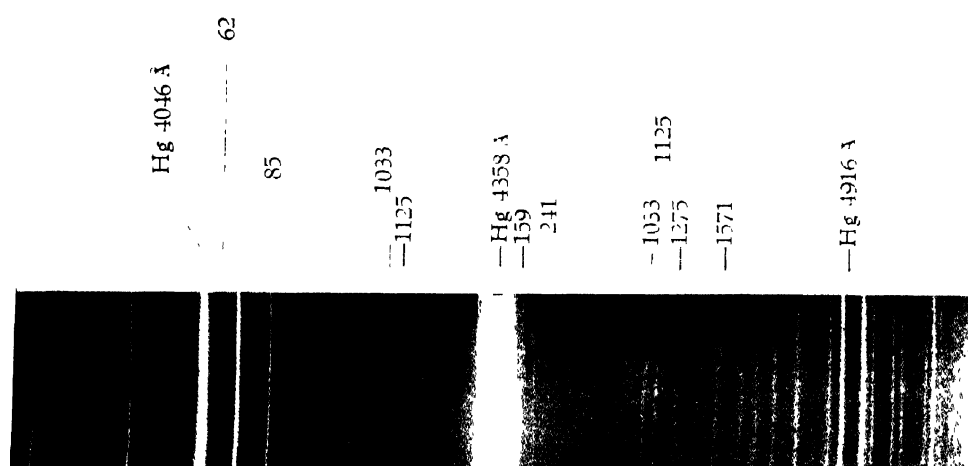
Raman shifts in wave numbers for thianthrene in the solid state

Raman shifts in cm^{-1}	Intensity	Assignment
85	4	A
159	4	A \pm
241	4	A
319	4	A
565	5	A
650	4	A
1033	10	A
1125	10	A
1275	4	A
1571	4	A
2462	2	A
2912	2	A
3044	6	A
62	2	B
85	2	B
561	4	B
1033	4 <i>bd</i>	B
1125	4	B

bd means broad and diffused

A = λ 4358 excitation

B = λ 4046 excitation



Raman spectrum of thianthrene in the solid state

The spectra were taken with a Fuess glass spectrograph having a dispersion of about 21 A.U. per mm in the λ_{4358} region. Ilford Selochrome plates were used and the exposures lasted for about 40 hours. The measurements were made with an accurate Zeiss Ikon Comparator and the wavelengths were calculated in the usual manner.

OBSERVATIONS AND DISCUSSIONS

It has been shown by Hendricks (1930) by X-ray measurements, that the simplest linear tricyclic hydrocarbon, anthracene, has all the 14 carbon atoms lying in the same plane, and that the two carbon atoms in para-positions in the central ring are also connected with each other as shown in the structural formula. From the mode of formation of anthracene, chemical evidence also verifies the same structural formula.

Thianthrene, which is the object of this investigation, differs from anthracene in this respect that the two CH groups of anthracene in the para-positions have been replaced by divalent atoms of sulphur. This substitution produces a reorientation of the valency bonds inside the molecule and gives quite different Raman frequencies from those of anthracene.

The central ring of thianthrene is not a benzene ring, but the other two rings are benzenoid in structure. Hence according to the Fixer rule, which states that the most stable form of a polynuclear hydrocarbon is that in which the maximum number of rings have the normal benzenoid arrangement of three double bonds, the compound should be only fairly stable. This is the reason why thianthrene begins to decompose when kept above its melting point for a few hours. The structural formula of thianthrene with all atoms lying in the same plane, gives the molecule a high degree of symmetry. Its two end rings have the same bond arrangement as the benzene molecule, so its Raman spectrum should have some frequencies due to the benzene rings, and a few others due to C-S linking.

As given in Table I, 14 Raman lines have been observed with thianthrene in the solid state, and four of these frequencies, *viz.*, 3044, 2462, 1571 and 1275 cm^{-1} respectively agree fairly well with the Raman frequencies of benzene. The frequencies, at 3044 cm^{-1} and at 2912 cm^{-1} may be taken to represent C-H vibrations, as no other type of vibration is expected to give the frequencies of this order. The frequency at 1571 cm^{-1} appears to be due to the C=C link of the benzenoid rings. A similar frequency at 1573 cm^{-1} occurs in naphthalene, which is slightly lower than C=C linkage in benzene occurring at 1596 cm^{-1} .

From the observations of the Raman shifts of thio-ethers, thio-acids and polysulphides, it is found that C-S shift falls near 645 cm^{-1} . Venkateswaran (1930) has shown that C-S shift in methyl mercaptan is 704 cm^{-1} which decreases to 659 cm^{-1} in ethyl mercaptan and to approximately 652 cm^{-1} in higher homologues. In thianthrene the carbon atoms connected

to the S atoms form part of a heavy ring, so the shift observed at 650 cm^{-1} may be due to C-S link. By comparing these Raman spectra with those of substituted benzene compounds it can be concluded that the frequencies at 1045 cm^{-1} and 1150 cm^{-1} relate to C-C link.

The frequencies observed at 319 cm^{-1} , 241 cm^{-1} and 159 cm^{-1} respectively in thianthrene containing condensed benzene rings, may be attributed to the deformational vibrations of the benzene rings against one another. Such low frequency lines are not generally observed in compounds possessing a single ring like benzene and its derivatives. The very low frequencies observed at 85 cm^{-1} and 62 cm^{-1} respectively may be attributed to the oscillations of the lattice. The substance has also been examined by us in the molten state (still unpublished) and it is found that the frequencies at 85 and 62 cm^{-1} completely disappear as the substance passed from the solid to the molten state. Hence, evidently, these two frequencies are due to the oscillations of the lattice.

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